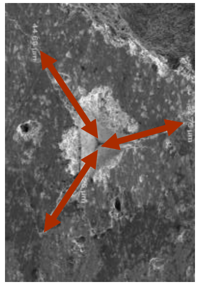
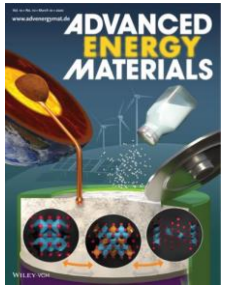
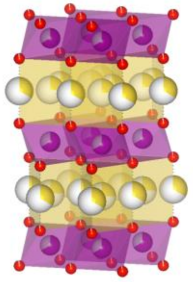
Sodium-Based Batteries







PRESENTED BY

Erik D. Spoerke, Ph.D.

DOE Office of Electricity Virtual Peer Review 2021
October 26-28, 2021

This work at Sandia National Laboratories is supported by Dr. Imre Gyuk through the U.S. Department of Energy Office of Electricity.

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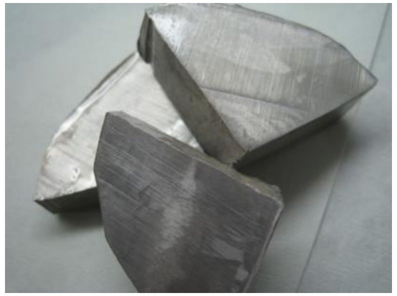
SAND No.: SAND2021-13478 C

Sodium Batteries: Diverse Technologies

Sodium batteries…

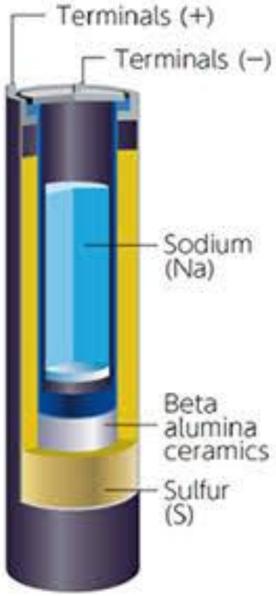
- Take advantage of globally abundant sodium…
  - 6th most abundant element in Earth's crust and 4th most abundant in the oceans.
  - 5X the annual production of aluminum
- Offer potential for safe, versatile, cost-effective energy storage
  - Grid-scale and backup power
  - Portable or vehicle storage



Sodium Metal

There are a number of sodium battery technologies in development or production:

1. Molten sodium (Na) batteries
   A. Sodium Sulfur (NaS)
   B. Sodium Metal Halide (Traditional ZEBRA Batteries)
2. Sodium Ion Batteries (NaIBs) – *PNNL, ORNL*
   A. "Li-Ion Analogs"
   B. Prussian Blue Analogs
   C. Salt-Water Batteries
3. Solid State Sodium Batteries (SSSBs)
4. Sodium Air Batteries ($Na-O_2$)



- Sodium Image from Dnn87 at English Wikipedia. - Transferred from en.wikipedia to Commons., CC BY-SA 3.0, https://commons.wikimedia.org/w/index.php?curid=3831512
- NaS battery schematic from NGK Insulators.

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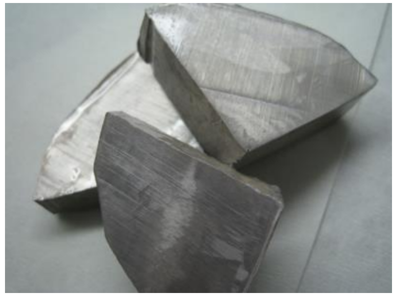

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   A. Sodium Sulfur (NaS)
   B. **Sodium Metal Halide (Traditional ZEBRA Batteries)**
      ✓ ***New ZEBRA Batteries (Ni-free, operate below 200°C) - PNNL***
      ✓ ***Low Temperature (~100°C) Na-NaI Batteries - SNL***
2. Sodium Ion Batteries (NaIBs) –
   A. *"Li-Ion Analogs" PNNL, ORNL*
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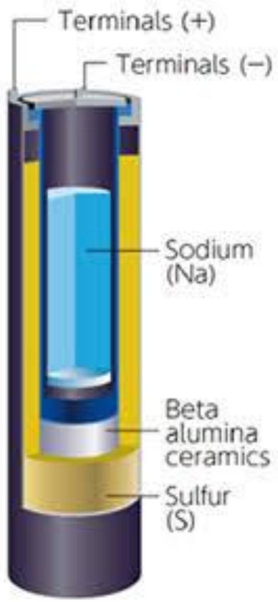

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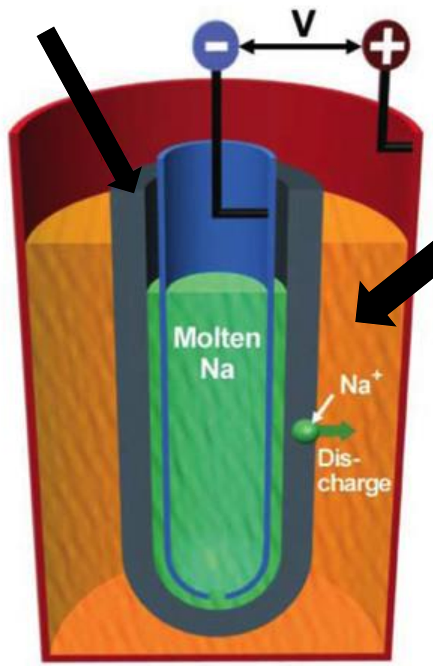
Molten Sodium Batteries: Where Does the Industry Stand?

Molten Sodium Battery Basics



Na-S

NGK INSULATORS

$xS + 2Na \leftrightarrow Na_2Sx$ ($3 \leq x \leq 5$) E_{cell} ~2.08 V at 350°C

✓ 600 MW/4.2 GWh of deployed storage in over 200 cites globally

$Na-NiCl_2$

FZSoNick

$NiCl_2$ (s) + 2Na (l) $\leftrightarrow$ 2NaCl + Ni (s) E_{cell} ~2.58 V at 300°C

✓ Approximately 130MWh deployed storage globally

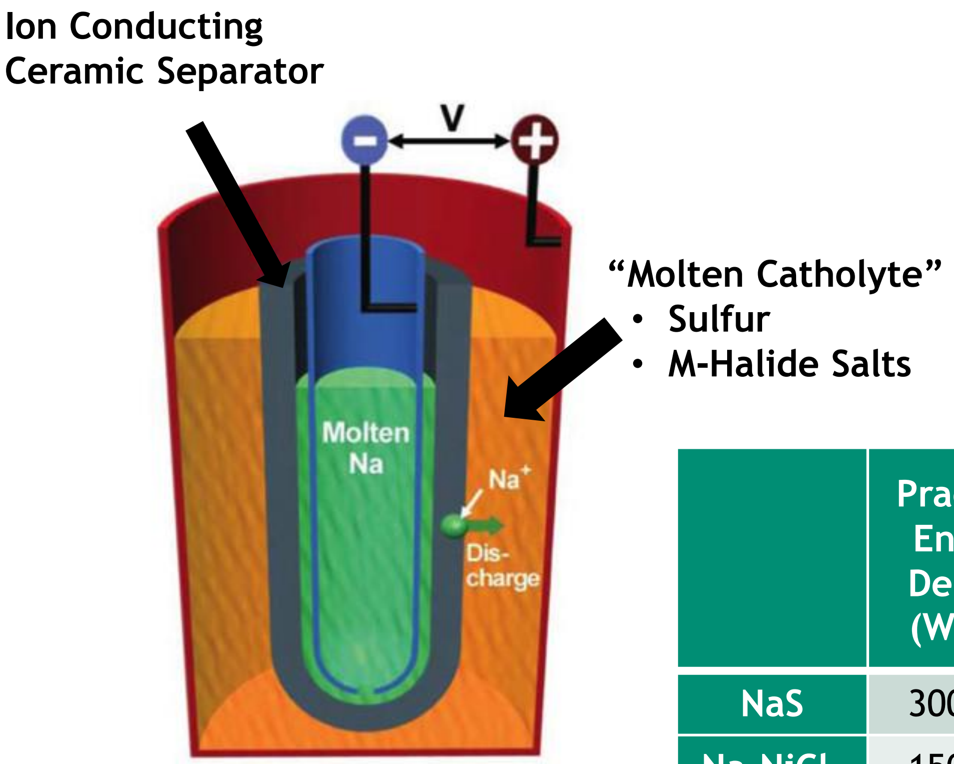
	Practical Energy Density (Wh/L)	Expected Cycle Life (cycles at 80% DOD)	Expected Lifetime (years)	Operating Temperature (°C)	Suitable Ambient Temperature (°C)	Discharge Duration (at rated power)	Round Trip Efficiency
NaS	300-400	4,000-4,500	15	300-350	-20 to + 40	6-7 hours	80%
$Na-NiCl_2$	150-190	3,500-4,500	20	270-300	-20 to +60	2-4 hours	80-85%

- Na-S takes advantage of low cost materials, but introduces some safety concerns.
- $Na-NiCl_2$ is a safer, greener chemistry, but high cost of Ni is a challenge.

NaS and $Na-NiCl_2$ batteries are used today for Renewables Integration, Grid Services, Consumer Applications, and Microgrids

Molten Sodium Batteries: Where Does the Industry Stand?

Molten Sodium Battery Basics



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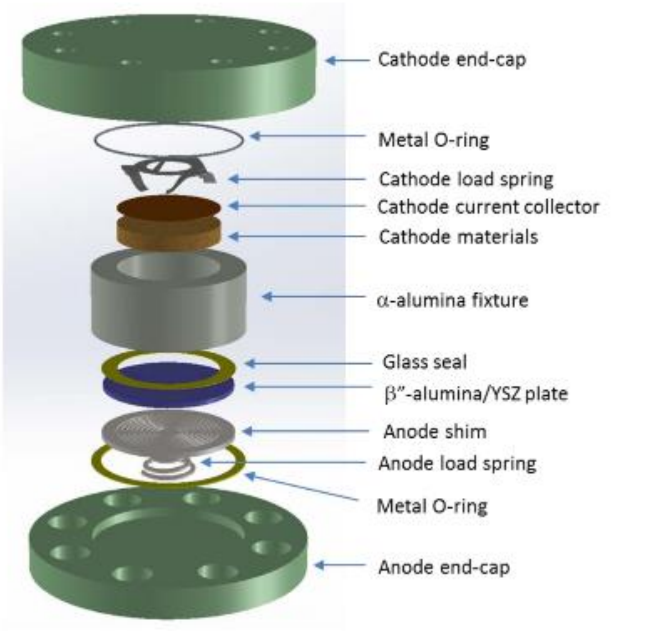
Lowering Battery Operating Temperature to Drive Down Cost

Our Collective OE Objective: A safe, reliable, molten Na-based that eliminates costly reagents (e.g., Ni) and operates at reduced temperatures (below 200ºC).

- Improved Lifetime
  - Reduced material degradation
  - Decreased reagent volatility
  - Fewer side reactions
- Lower material cost and processing
  - Seals
  - Wiring!
  - Cell body
  - Polymer components?
- Simplified heat management costs
  - Operation
  - Freeze-Thaw

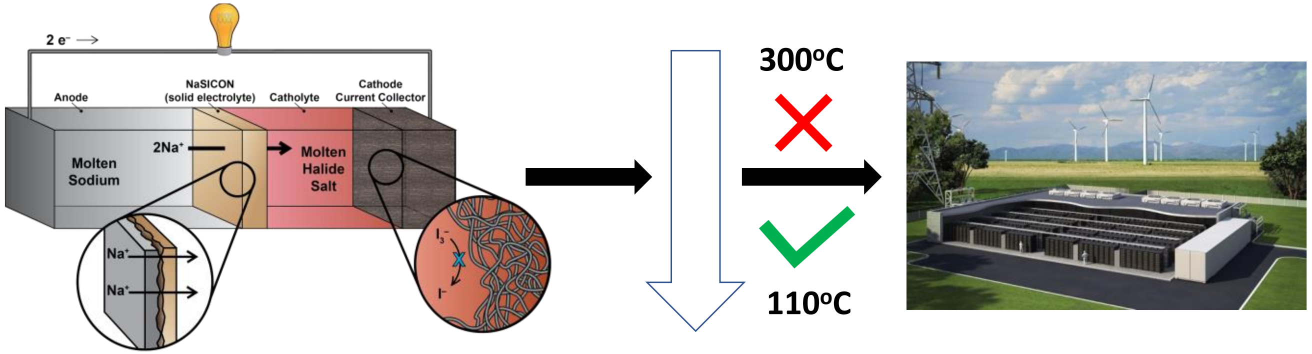
PNNL intermediate temperature (<200ºC) planar Na-MH battery design.

FY21 focus on using low cost cathode materials (Fe, etc) to replace Ni.



Li, G, et al. *Nature Commun*. **2016**, *7*, 10683.

SNL design for Na-NaI low temperature (~100ºC) battery



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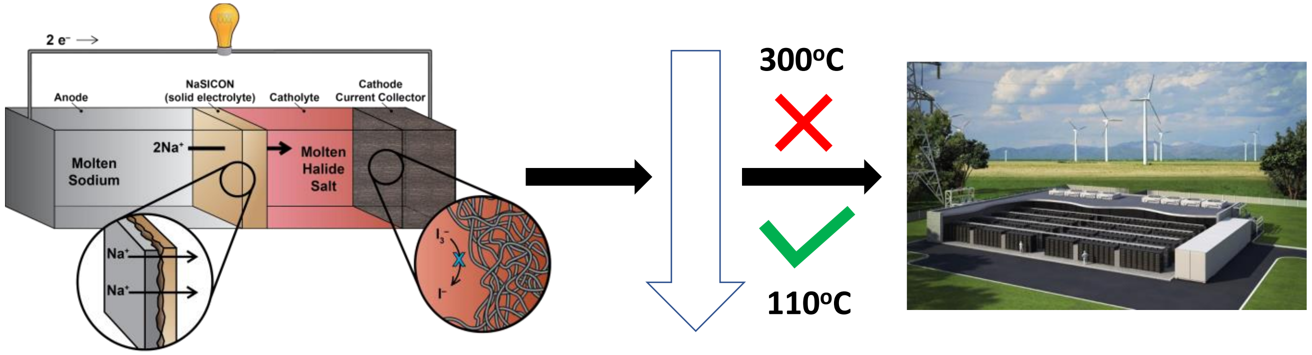
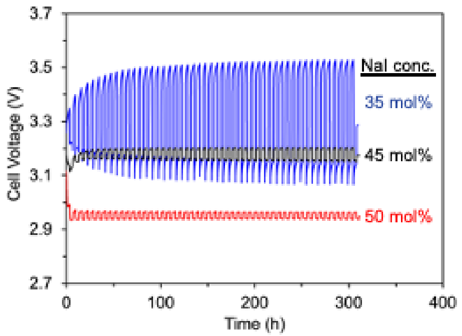
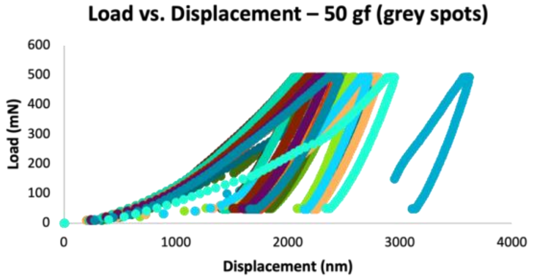


FY21 Focus Areas:

- Realizing high performance with lower-cost catholytes
- Improving NaSICON Production/Performance
- Exploring mechanical properties of NaSICON (U. Kentucky, Prof. YT-Cheng)

Cycling with new catholytes





Considerations in Na-Ion Battery Development

Resource	Crustal Abundance	Distribution	Price US$/kg
Na	2.75%	Everywhere	0.3 (Na_2CO_3)
Li	0.0065%	75% in Americas	20 (Li_2CO_3)

Current Collector

NIBs: Al foil (cheap) for both positive and negative electrodes

LIBs: Cu foil (expensive) for negative and Al foil for positive

Cost of NIBs vs. Cost of LIBs

Cost of NIBs is 30~40% cheaper ↓↓↓

Tips: NaCuFeMnO and Soft-Carbon are used in NIBs; $LiFePO_4$ and Graphite are used in LIBs.

	LABs	<	SIBs	<	LIBs
Energy Density	30~50 Wh/kg		100~150 Wh/kg		150~250 Wh/kg
Voltage	~2.1 V		2.8~3.5 V		3.0~4.5 V
Life	~300 cycles		2000+ cycles		3000+ cycles

Tips: The above parameters of different materials varies.

NIBs can be fully discharged for shipping, LIBs must be maintained at 30% SOC.

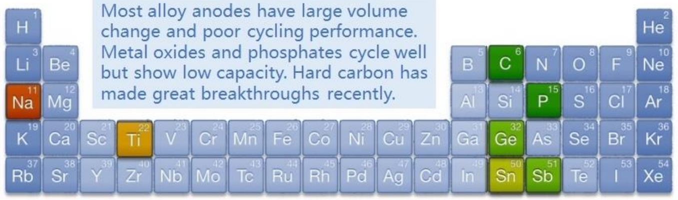
Anode Materials for NIBs

Transition Metals Are Dispensable for Anodes.

100+ Anode materials have been reported:

- Carbon (e.g. hard/soft carbon)
- Alloy (e.g. Sn, Sb, SnSb)
- Transition Metal Oxides (e.g. $Na_{0.66}Li_{0.22}Ti_{0.78}O_2$)
- Transition Metal Phosphates (e.g. $NaTiOPO_4$)

Longer Cycling Life
Lower Cost
Faster Charge/Discharge



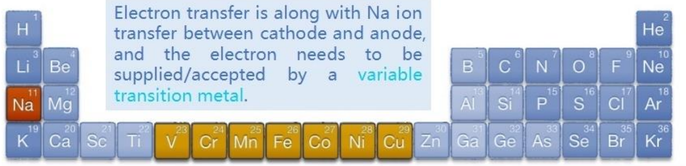
Cathode Materials for NIBs

Different Structure, Indispensable Transition Metals

100+ cathode materials have been reported:

- Transition Metal Oxides (e.g. $NaMnO_2$)
- Transition Metal Phosphates (e.g. $Na_3V_2(PO_4)_3$, $Na_2MnP_2O_7$)
- Transition Metal Sulfates (e.g. $Na_2Fe_2(SO_4)_3$)
- Transition Metal Cyanates (e.g. $Na_2FeFe(CN)_6$)

Higher Energy Density
Longer Cycling Life
Lower Cost



Application of NIBs

- Global sodium-ion batteries market has been estimated to reach USD 1.01 billion in 2021.
- Projected to grow at a CAGR of 19.3% during the forecast period from 2021-2030.

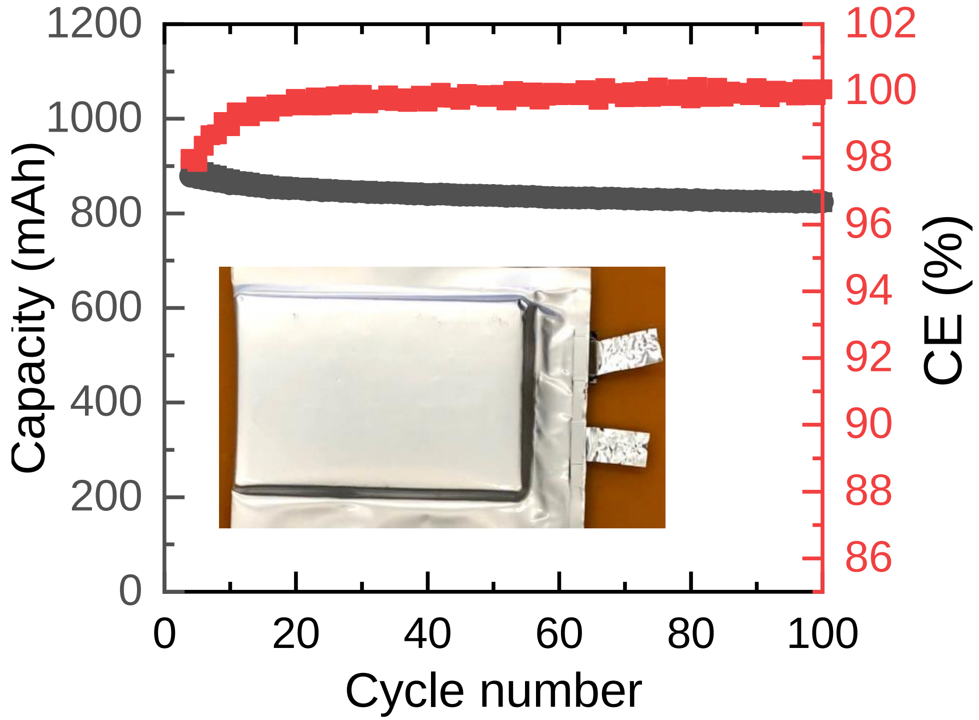
Quince Market Insights, 2021

Slide data from https://www.hinabattery.com/en/index.php?catid=12

Na-Ion Batteries: Development and Scale-up of Advanced Cathode Materials (PNNL)

Pacific Northwest NATIONAL LABORATORY

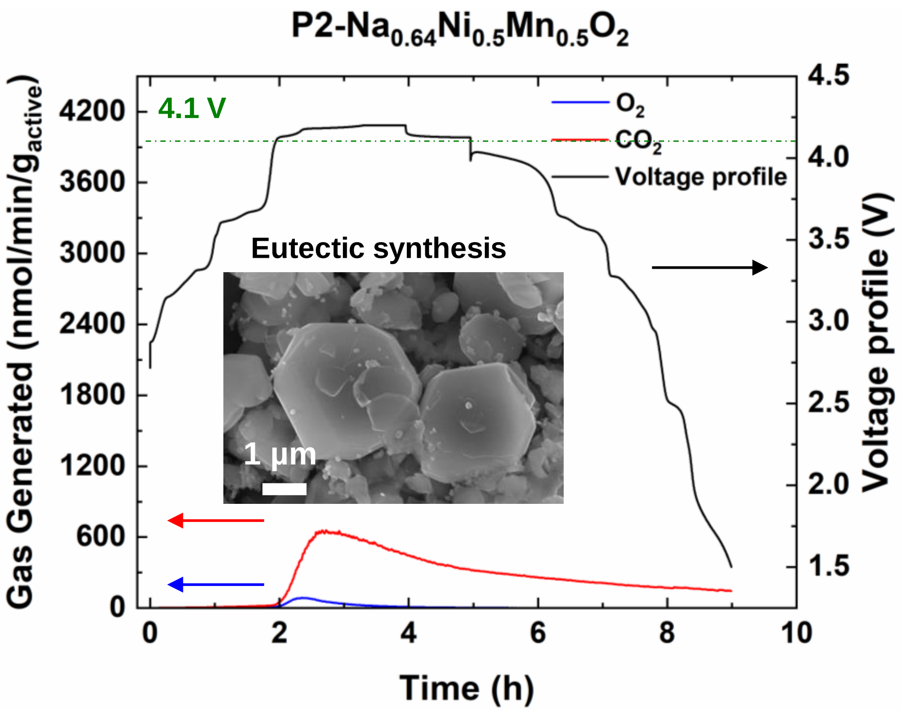
Project Highlights

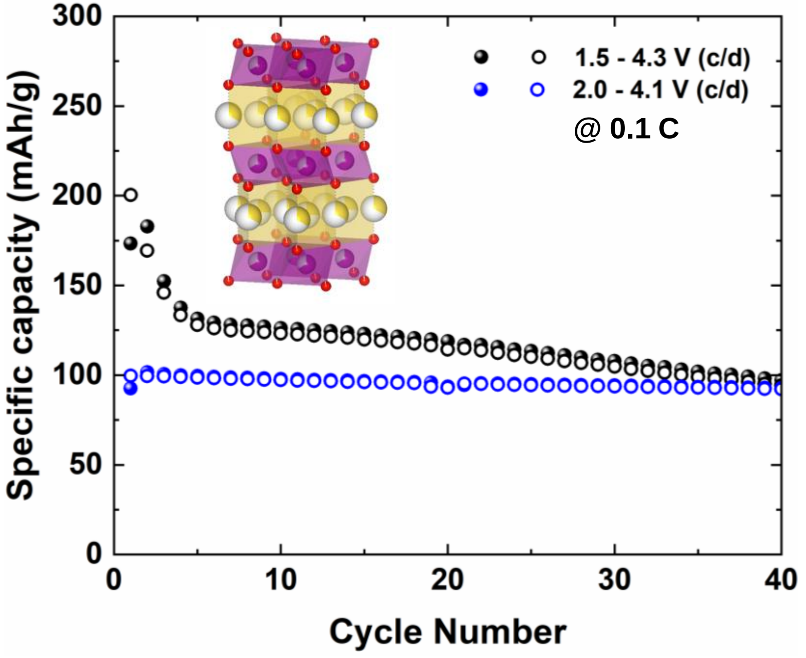


- Gen 2 (Ni-rich NMC cathode) material synthesis scaled up to 1 kg/batch level, multi-layer pouch cell assembly was scaled up to ~ 1Ah.
- Gen 3 (Ni-low, Co-free cathode) material synthesis scaled up to 50g/batch, single-layer pouch cell assembly achieved 50 mAh.
- Discovered new mechanisms for promoting cathode performance.

Biwei Xiao

Novel Cathode Synthesis and Gassing Studies (ORNL)





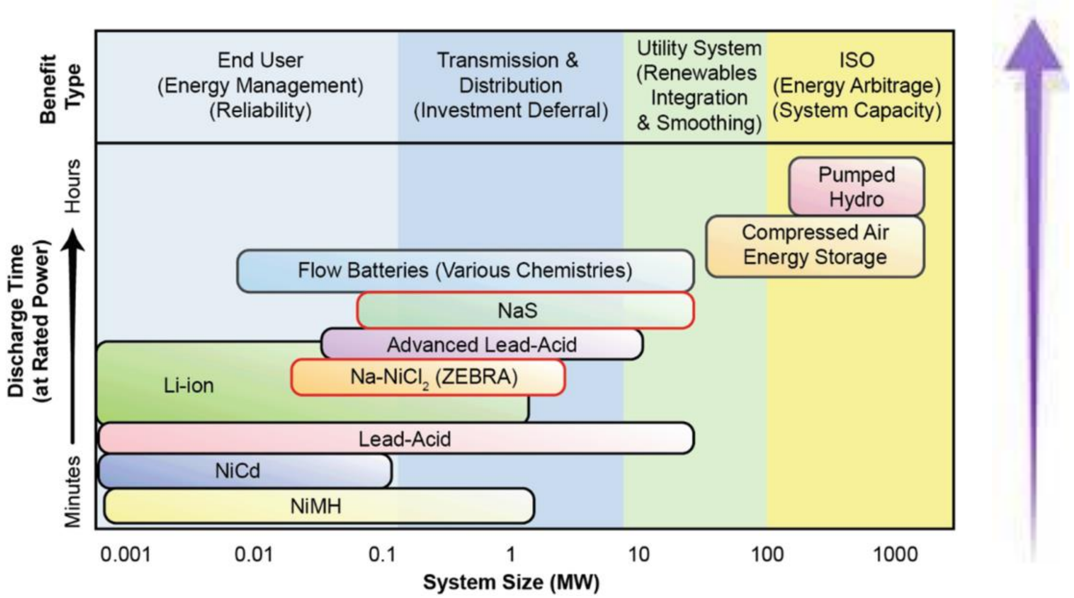
- ORNL's Belharouak team developed novel eutectic synthesis for sodium transition metal layered oxide cathodes.
- Gassing studies were performed to evaluate the oxygen anion redox in different kinds of cathodes in pouch cells and seek engineering routes towards longer duration storage and stable cycling performances.

Looking to a Future with Long-Duration Energy Storage

Long-Duration Energy Storage (>10 hours) continues to be a growing priority for the DOE Office of Electricity's Energy Storage Research Program and across the DOE.

What are the Roles for Batteries in Long-Duration Energy Storage?

- Lithium-Ion Batteries
- Sodium-Based Batteries
- Zn-Based Batteries
- Flow Batteries
- Pb-Acid
- Metal-Air Batteries



Seasonal

Long-Duration

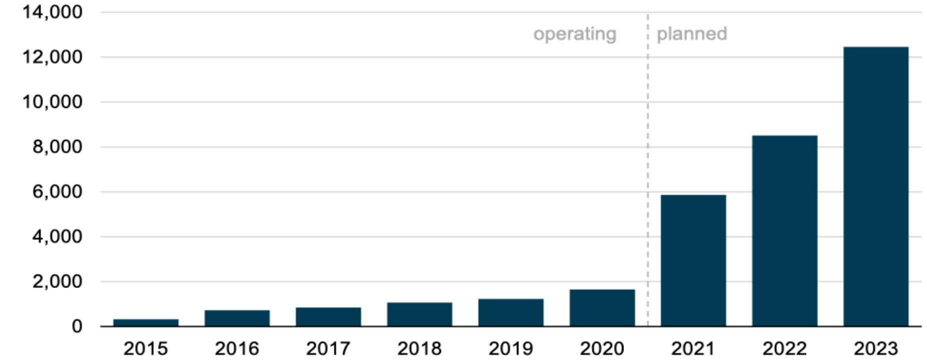
Medium-Duration

Short Duration

AUGUST 20, 2021

U.S. large-scale battery storage capacity up 35% in 2020, rapid growth set to continue

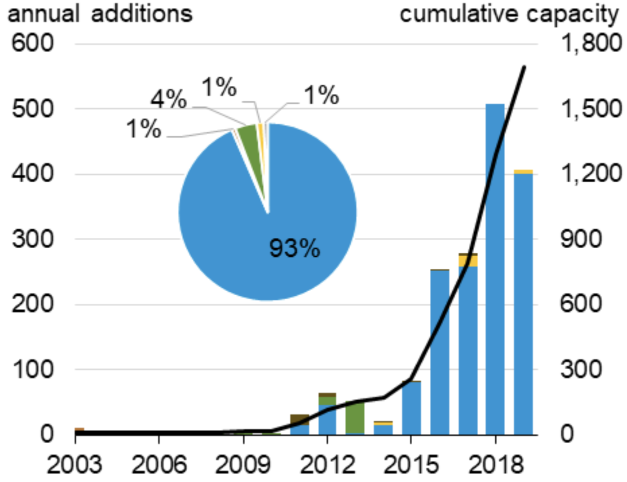
U.S. large-scale battery storage power capacity (2015–2023)
megawatts



Source: U.S. Energy Information Administration, *Preliminary Monthly Electric Generator Inventory*, December 2020

energy capacity (MWh)

lithium-ion
nickel-based
sodium-based
flow
other



Source: U.S. Energy Information Administration, 2019 Form EIA-860, *Annual Electric Generator Report*

Looking to a Future with Long-Duration Energy Storage

Emerging Efforts:

- All Soluble Iron Flow Battery (PNNL)
  - all soluble Fe flow battery (intends to replace vanadium) for long duration and thermocycling battery (reduces self-discharge) for seasonal storage.

- Earth Abundant Molten Salt Batteries (SNL)
  - Utilize low-carbon approach to scalable molten salt batteries based on earth-abundant active materials.

The DOE OE program has the opportunity to build on current programs to meet critical LDES needs!

More LDES Content!

DOE Long-Duration Energy Storage Workshop

“BIG” Energy Storage:
Priorities and Pathways to Long-Duration Energy Storage

Sandia National Laboratories
Pacific Northwest NATIONAL LABORATORY
OAK RIDGE National Laboratory

longdurationstorage.sandia.gov

- **Posted presentations**
- **Issue Brief on Long-Duration Energy Storage (as of late 2020)**
- **Recorded presentations available**
    - Use Cases
    - Policy
    - Economics
    - Technologies

Contact:
edspoer@sandia.gov

On to the Main Show: Presentations

Sodium				
10:35 – 10:50 AM	**Program Overview**	**Erik Spoerke (Session Lead)**	**Sandia National Laboratories**	**300**
10:50 – 11:05 AM	Low Temperature Molten Sodium Batteries	Leo Small	Sandia National Laboratories	301
11:05 – 11:20 AM	Mechanical, Microstructural, and Electrochemical Characterization of NaSICON Sodium Ion Conductors	Yang-Tse Cheng	University of Kentucky	302
11:20 – 11:35 AM	(I) Intermediate Temperature Na Battery Technologies (II) Long Duration/Seasonal Battery Development	Guosheng Li	Pacific Northwest National Laboratory	303
11:35 – 11:50 AM	Na-ion batteries: Development and Scaling-up of Advanced Cathode Materials	Biwei Xiao	Pacific Northwest National Laboratory	304
11:50 AM – 12:05 PM	Deep Dive into the Oxygen Anion Redox in Na Layered Oxide Cathodes Synthesized by Eutectic	Ilias Belharouak	Oak Ridge National Laboratory	305
12:05 – 12:20 PM	**Break**			
12:20 – 01:00 PM	**Roundtable: Long Duration Energy Storage**			

Please Don't Miss: Posters

Institution	Title	Authors
Sandia National Laboratories	Low-Temperature Molten Sodium Batteries	Martha M. Gross, Stephen J. Percival, Amanda S. Peretti, Joshua Lamb, Erik D. Spoerke, Leo J. Small
University of Kentucky/Sandia National Laboratories	Mechanical, Microstructural, and Electrochemical Characterization of NaSICON Sodium Ion Conductors	Ryan C. Hill, Jacob Hempel, Yang-Tse Cheng, Leo Small, Erik D. Spoerke, Martha M. Gross, and Amanda Peretti.
Pacific Northwest National Laboratory	Feasibility of Na-FeCl2 Batteries for Long Duration Energy Storage Applications	Evgueni Polikarpov, Xiaowen Znan, Miller Li, J. Mark Weller, Keesung Han, David Reed, Vincent Sprenkle, and Guosheng Li
Pacific Northwest National Laboratory	Advancing Low Cost, Intermediate Temperature Na-Al Batteries for Scalable Long-Duration Energy Storage	Jon (Mark) Weller, Mark H. Engelhard, David M. Reed, Vincent L. Sprenkle, and Guosheng Li